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IMMERSION PLATING WITH NOBLE METALS

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This is a continuation-in-part of my co-pending application Serial No. 653,286, filed April 17, 1957.

The present invention relates to immersion gold plating and more particularly to an immersion gold plating bath and a method for plating metallic articles with gold utilizing such bath.

Immersion plating of metals heretofore practiced has been somewhat limited because of the absence of a desirable plating solution or bath. Plating solutions of known composition suffer from rapid undesirable contamination by the replaced metal, resulting in poor adherence or non-uniform deposits on the metal being plated. For example, immersion plating of gold on nickel with the use of conventional immersion plating solutions results in poor adherence of the gold and with the gold film having a brownish appearance instead of the desirable bright yellow gold appearance.

Immersion plated films or layers are of greater density than electroplated films or layers and as such have greater corrosion and wear resistance than electroplated films of equal thickness.

With the use of immersion plating baths herein contemplated, the plated articles are provided with uniform thickness deposits regardless of surface concavity and indentation or uneven article contour and configuration as opposed to non-uniform electroplated deposits, since the electroplated deposits are heavier on the higher electric density areas of the cathode.

It is an object of this invention to provide an immersion gold plating bath capable of depositing bright gold films on a suitable metal base.

Another object of this invention to provide an immersion gold plating bath which operates at peak efficiency regardless of the build-up of concentrations of displaced metals going into solution during the plating process.

A further object of this invention is to provide an immersion gold plating bath capable of use for plating metallic articles with gold films of bright yellow appearance with a gold concentration of the bath as low as 10 milligrams of soluble gold salt per liter.

Other objects and advantages of the invention will become apparent from the following description.

In accordance with the present invention, new and improved immersion gold plating baths are provided which result in deposition of gold films on the articles being plated which have a desirable bright yellow gold appearance as contrasted with the gold films of brownish appearance of the prior art gold plating baths. Further, the gold films deposited by the plating solutions of this invention are of uniform or substantially uniform thickness and show good adherence to the articles being plated. The immersion gold plating bath of this invention consists essentially of water, a soluble gold salt, preferably sodium gold cyanide or potassium gold cyanide, an ammonium buffering agent, and an organic chelating agent. The pH of the bath is essentially maintained at a pH of between 5.5 and 14.

The metal article or substrate being plated is provided with a coating or film of gold in accordance with this invention by reason of replacement of metal atoms on the surface of the metallic article being plated by gold ions, with the replaced metal atoms passing in ionic form into solution in the bath. The chelating agent ties up or chelates these replaced surface metal ions thereby preventing

such metal ions from interfering with the gold plating, and hence preventing the undesirable brownish appearance of the deposited gold films as well as the poor adherence and non-uniform thickness of the films attendant with use of the prior art plating solutions.

The gold plating baths or solutions of this invention are capable of use for plating metallic articles with uniform gold films or bright yellow appearance and which show good bonding to the article with a concentration of gold salt in solution as low as 10 milligrams per liter due to the progerssive build-up of impurities therein due to the replaced metal going into solution. This was unexpected and surprising inasmuch as with the immersion plating baths of the prior art, one could only plate about 50% of the gold out of the bath with satisfactory results.

The pH of the gold plating solution is maintained at between 5.5 and 14 inasmuch as at a pH of the bath much below 5.5, its stability is poor. A preferred pH for plating gold on nickel and nickel-base alloys is between 5.5 and 10. A preferred pH for plating gold on copper is pH 6–7. For plating gold on tungsten a preferred pH is 13–14.

The ammonium buffering agent serves to regulate or maintain the pH of the plating bath at the particular pH desired within the pH range previously disclosed herein. In addition, the ammonium buffering agent exerts a complexing action to complex a portion of the replaced metallic ions from the surface of the metal article being plated. Ammonium buffering agents suitable for use herein are ammonium salts of weak acids such as, for example, the ammonium salts of hydroxy organic acids having 2–3 carboxyl groups per molecule, e.g., ammonium tartrate and ammonium citrate; ammonium borate, ammonium gluconate, and ammonium acetate. Ammonium tartrate and citrate are preferred. These agents can be added as such or formed in situ in the bath. The complexing action on some of the replaced metallic ions by the ammonium buffering agent is illustrated in the immersion gold plating of copper in accordance with this invention, wherein a portion of the replaced copper ions are more readily complexed with the ammonium citrate than with the chelating agent due to the quicker reaction with the citrate to form the complex, copper ammoniacal citrate. The chelating agent then chelates the remaining portion of the copper ions not complexed by the ammonium citrate. Further, in the plating of copper-base alloys, e.g., brass; nickel, nickel alloys, iron and steel, it is important to have the complexing activity of the ammonium buffering agent in the bath as well as the chelating action of the chelating agent, with the ammonium buffering agent complexing a portion of the metal ions of the metals replaced by the gold ions in addition to performing its important function of maintaining the pH of the solution within the range previously stated, and the chelating agent tieing up or chelating the remainder of these replaced metal ions. Additionally, the ammonium buffering agent may serve to accelerate the plating by attacking the surface metal of the article to be plated. For instance, in plating iron and nickel, the ammonium citrate is believed to attack both of these metals to some extent to apparently displace metallic ions from the surface of these metals, with the gold ions replacing an equivalent amount of the removed iron or nickel ions. Ammonium tartrate is superior to ammonium citrate in the plating of lead and lead base alloys in accordance with this invention but is not as good as ammonium citrate in the plating of iron and nickel. The term "ammonium buffering agent" is used herein and in the appended claims to mean the ammonium salt of a weak acid, for instance ammonium citrate, ammonium tartrate, ammonium borate, ammonium gluconate, or ammonium acetate, which serves to main-

tain or regulate the pH of the plating solution of this invention within the pH range previously disclosed herein and which in addition, chemically complexes a portion of the replaced metal ions from the surface of the metallic article being plated.

Exemplary of the organic chelating agents utilizable in the plating bath for chelating the replaced metal ions are ethylenedinitrilo tetraacetic acid and the di-sodium, tri-sodium and tetra-sodium salts of the ethylenedinitrilo tetraacetic acid, urea, cyanoacetamide, dicyandiamide, ethylenediamine and ethyl acetoacetate. The ethylenedinitrilo tetraacetic acid and its di-, tri- and tetra-sodium salts are the preferred chelating agents with the tri- and tetra-sodium salts being preferred among these as each is highly soluble in water.

The soluble gold salt is present in the plating bath or solution of this invention in amount of about 20 milligrams to about 30 grams per liter, preferably about 100 milligrams to 5 grams per liter. The ammonium buffering agent is present in the plating bath in amount of about 80 milligrams to about 120 grams per liter, preferably about 400 milligrams to about 20 grams per liter. The chelating agent is present in the bath in a weight ratio of chelating agent to soluble gold salt within the ratio range of preferably about 3:1 to about 8:1 respectively, more preferably about 5:1 respectively. By the term "organic chelating agent" as used herein and in the appended claims is meant an organic compound, for instance an organic compound previously disclosed herein as chelating agent, which will chemically unite with the replaced metal ions in solution from the surface of the metallic article being plated to prevent these metal ions from interfering with the gold plating of the metallic article, i.e., from causing a brownish or other off-color appearance to the deposited gold film when a bright yellow gold film is desired, and also from causing poor adherence of the gold film to the metallic article surface and gold films of non-uniform thickness. In chelating, the chemical union is usually of the type wherein the metal atom is joined as a central atom to other atoms in the same molecule by both ordinary and coordinate valence forces. The term "organic chelating agent" used herein and in the appended claims does not include the ammonium buffering agent.

The following are examples of plating baths of this invention, on a one liter basis.

BATH 1

	Grams
$KAu(CN)_2$	5
Ammonium citrate	20
Urea	25
Water, 1 liter.	

BATH 2

$KAu(CN)_2$	5
Ammonium citrate	20
Ethylenedinitrilo tetraacetic acid	25
Water, 1 liter.	

BATH 3

$KAu(CN)_2$	5
Ammonium citrate	20
Ethylenedinitrilo tetraacetic acid (tetra sodium salt)	25
Water, 1 liter.	

BATH 4

$KAu(CN)_2$	5
Ammonium citrate	20
Acetamide	25
Water, 1 liter.	

BATH 5

$KAu(CN)_2$	5
Ammonium citrate	20
Cyanoacetamide	25
Water, 1 liter.	

BATH 6

$KAu(CN)_2$	5
Ammonium citrate	20
Dicyandiamide	25
Water, 1 liter.	

BATH 7

$KAu(CN)_2$	5
Ammonium citrate	20
Sulfosalicylic acid	25
Water, 1 liter.	

BATH 8

$KAu(CN)_2$	5
Ammonium citrate	20
Urea	25
Ammonium hydroxide to pH 9–10.	

BATH 9

$KAu(CN)_2$	5
Ammonium citrate	20
Ethylenediamine	25
Water, 1 liter.	

BATH 10

$KAu(CN)_2$	5
Ammonium citrate	20
Ethyl acetoacetate	25
Water, 1 liter.	

BATH 11

$KAu(CN)_2$	5
Ammonium citrate	20
Urea	25
Ethylenedinitrilo tetraacetic acid (tetra sodium salt)	15
Water, 1 liter.	

The urea, ethylenedinitrilo tetraacetic acid, cyanoacetamide, dicyandiamide, ethylenediamine, ethyl acetoacetate, and the tetra sodium salt of ethylenedinitrilo tetraacetic acid of respectively Baths 1, 8 and 11, 2 and 3, 5, 6, 9, 10 and 11 function to chelate the replaced metal ions from the surface of the article being plated to obviate or prevent interference by these metal ions with the gold plating of the metallic article with the undesirable results previously mentioned herein. The acetamide and sulfosalicylic acid of Baths 4 and 7 respectively may or may not form chelate bonds with the replaced metal ions, but in any case serve to chemically complex the replaced metal ions from the surface of the article being plated to prevent the undesirable interference with the gold plating.

The preferred temperature of the gold plating bath for plating is from about 40° C.–100° C. While bath temperatures considerably below 40° C. can be used, these lower temperatures are not preferred because the gold deposition is slow. For instance, while gold plating to an appreciable deposit occurs at a bath or solution temperature of 20° C., the plating time is about 1 hour. However, at a bath temperature of 100° C. the plating time is usually less than 1 minute, and at a bath temperature of 60° C. a plating time of about 3 minutes is required for the same thickness deposit. At 40° C., the plating bath requires about 15 minutes for effecting the same thickness deposit of gold on the metallic article.

The following are examples of plating processes according to the invention:

Example I

A plating solution was prepared by dissolving 5 grams of potassium gold cyanide in 30 cc. of 28 percent ammonium hydroxide. Water was added to make a 1 liter volume. To the ammoniacal gold cyanide solution, 25 grams of ethylenedinitrilo tetraacetic acid (tetra sodium salt) were added. Citric acid was then added in sufficient quantity to adjust the pH to 6.5, which resulted in the presence of about 10 grams of ammonium citrate per liter. The solution was heated to 70° C. A 1" x 3.5" x 0.010"

strip of nickel plated brass was degreased with carbon tetrachloride vapor and then electrocleaned cathodically in a boiling solution of trisodium phosphate. The strip was then washed with water and immersed in the plating solution for 3 minutes. After removal from the plating solution, the gold-deposited strip was dried. The difference in weight before immersion and after immersion indicated a gold deposit of about 0.000005" thickness on the strip.

Example II

An immersion gold plating bath was prepared having the following composition:

	Grams
$KAu(CN)_2$	1500
Ethylenedinitrilo tetraacetic acid	6000
Ammonium citrate	8000

Water, 300 liters.

The pH of the above bath solution was approximately 8. This bath was used to gold plate lead-tin alloy trophies having an electroplate of copper over the alloy in the following manner. After the usual plating of a bright nickel electroplate on the copper of the trophies, the trophies were removed from the electroplating bath, washed with water, and immediately transferred from the washing bath and immersed in the gold plating bath. The trophies were kept immersed in the gold plating bath at a bath temperature of 80° C. for 1½ minutes, then removed, washed with water and dried. This immersion plating produced a brilliant 24 carat yellow gold surface that was of uniform color regardless of the configuration of the trophy. The bath plated 15,360 square feet of trophies before becoming, for practical purposes, exhausted of gold. The gold content of the plating bath at the point of exhaustion for commercially practical plating was .009 troy ounce of gold per gallon.

Example III

A plating bath for the immersion plating of gold was prepared having the following composition:

	Grams
$KAu(CN)_2$	750
Ammonium citrate	4000
Ethylenedinitrilo tetraacetic acid	3000

Citric acid to adjust to pH 7.
Water, 150 liters.

This bath solution was used to deposit gold on copper printed circuit boards for purposes of providing tarnish-free shelf life and good solderability of the printed circuits. The boards were first scrubbed with pumice to remove dirt and photo resist and washed with cold water. The boards were then immersed in the gold plating bath at a bath temperature of 75° C. for 5 minutes, after which they were removed from the bath, rinsed in running water and dried. A uniform gold deposit of .000002" thickness was obtained in the copper. Further time in the bath resulted in no further change in the deposit thickness. The plating bath produced 8000 square feet of gold-plated copper representing approximately 24,000 square feet of circuit boards.

The gold deposits provide a uniform gold coating which

is integral with the metal base over which it is plated. By integral is meant that the bond or adhesive strength between the coat and base is at least equal to the cohesive strength of the coating.

It has been found that gold may be deposited on a wide range of metal bases which includes the metals nickel, nickel alloys, copper and copper alloys, tungsten, cadmium, zinc, aluminum and aluminum alloys, silver alloys, iron, steel, die cast metals, solders, pewter and Alumel. The articles so plated include among others costume jewelry, trophies, automobile trim, lamp components, clock components, photo frames, bottle caps, radio knobs, metallized plastic components, electrical plug connectors, etc. Also, the solution may be used for color coating and for providing an intermediate layer for a subsequently applied second metal coat.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. An ionic replacement immersion gold plating bath consisting essentially of water, about 20 milligrams to about 30 grams per liter of a soluble gold salt selected from the group consisting of sodium gold cyanide and potassium gold cyanide, about 80 milligrams to about 120 grams per liter of an ammonium salt of a weak acid, and a water-soluble organic chelating agent present in amount within the weight ratio range of chelating agent to soluble gold salt of about 3:1 to about 8:1 respectively, the bath having a pH between 5.5 and 14.

2. The immersion gold plating bath of claim 1 wherein the ammonium salt is ammonium tartrate.

3. The immersion gold plating bath of claim 1 wherein the ammonium salt is ammonium citrate.

4. The immersion gold plating bath of claim 1 wherein the chelating agent is the tetrasodium salt of ethylenedinitrilo tetraacetic acid.

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